STUDIES ON THE SYNTHESIS AND STABILITY RELATIONS OF ZEOLITES Y AND P USING RICE HUSK ASH

By

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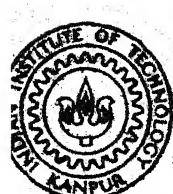
DEPARTMENT OF CHEMICAL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY, KANPUR

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STUDIES ON THE SYNTHESIS AND STABILITY RELATIONS OF ZEOLITES Y AND P USING RICE HUSK ASH

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CERTIFICATE

Certified that the work "STUDIES ON THE SYNTHESIS AND STABILITY RELATIONS OF ZEOLITES Y AND P USING RICE HUSK ASH" by Sri P M. Satya Sai has been carried out under our supervision and that this work has not been submitted elsewhere for a degree.

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ABSTRACT

The present study deals with the synthesis and stability aspects of zeolites Y and P in the temperature ranges 60-100°C with the reaction time varying from 12 to 72 hours in the compositional ranges of Na_2O/Al_2O_3: 4 to 9, SiO_2/Al_2O_3 : 2 to 22 using 90 - 95 molar per cent water for the starting mix. A total of 200 experimental runs for the hydrothermal synthesis have been conducted using an autoclave of high pressure type (Parr make). All the products obtained on synthesis have been characterized using x-ray diffraction technique. For the first time the author has used rice husk ash as one of the sources of silica in conjunction with silica gel for the synthesis of these two zeolite species. Distinct patterns of crystallization of zeolites Y and P_C as a function of the composition of the initial mix and the reaction temperature have been established. It has been observed that the rate of formation of zeolite P_C in its association with zeolite Y in the synthesis products increases with the increase in reaction temperature Both the zeolites Y and P_C convert into the species analcime with the reaction temperature approaching 100°C.

CHAPTER 1

INTRODUCTION

Zeolite molecular sieves have a wide range of applicability in modern industry. The discovery of this class of materials resulted in a wide scientific interest and Kaleidoscopic development of applications compared to many other inorganic materials.

McBain (1932) introduced the term "molecular sieve" to define porous solid materials, which exhibit the property of acting as sieves on a molecular scale. Zeolite molecular sieves have pores of uniform size which are uniquely determined by the unit structure of the crystal. These pores completely exclude molecules which are larger than their diameter. On the other hand, activated carbons and activated alumina and silica gel do not possess an ordered crystal structure resulting in the nonuniformity of pores. At present, the most important molecular sieve effects are shown by dehydrated crystalline zeolites These materials all have or high internal surface area available for adsorption due to the channels or pores which uniformly penetrate the entire volume of the solid. The external surface of the adsorbent particles contributes only a small amount of the total available surface area.

Zeolites are crystalline, hydrated aluminosilicates of group I and group II as they are found in nature or synthesized. The other categories like rare earth zeolites are obtained by ion exchange. The most important zeolites are of sodium, potassium, magnesium, calcium, strontium and barium.

Zeolites can be represented by the generalized formula

$$M_{2/n}O \cdot Al_2O_3 \cdot x\ SiO_2\ yH_2O$$
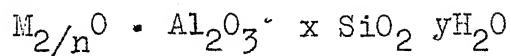
where M is the cation with a valency n and x is generally 2 since AlO_4 tetrahedra are joined only to SiO_4 tetrahedra. The framework contains channels and interconnected voids which ar are occupied by the cation and water molecules.

Application of Zeolites:

Zeolites have a wide variety of applications as the separation and recovery of normal paraffin hydrocarbons, catalysis of hydrocarbon reactions, many uses in drying such as for the drying of refrigerants; as adsorbents in the separation of air components and for the production of oxygen enriched streams; in the recovery of radioactive ions from radioactive waste solutions; in the removal of carbon dioxide and sulphur compounds from natural gas and the control of air pollution.

Molecular sieves are also utilized for separations on a commercial scale in the industries such as, petroleum

refining in catalytic cracking, hydrocracking, alkylation, isomerization, catalytic reforming, catalytic polymerization, vapor recovery, heavy products finishing and light products finishing; chemical and petrochemical industries producing ammonia, hydrogen, sulphuric acid, unsaturated hydrocarbons, biodegradable detergents and aromatics; in removal or separation of atmospheric gases as oxygen, nitrogen and argon and in natural gas industry during production, processing, transmission and storage.

Application of Synthetic Zeolites as Molecular Sieves:

The two major applications of synthetic zeolites are in adsorption and catalysis.

For Adsorption:

The zeolites are high capacity, selective adsorbents for two reasons:

1. They separate molecules based upon molecular size and configuration of the molecule relative to the size and geometry of the zeolite structure.

2. They adsorb molecules, in particular, those with a permanent dipole moment and other interaction effects, with a selectivity that is not found with conventional adsorbents.

In the process two types of separation may occur -- one based on molecular sieve effect and other on preferential adsorption.

As Catalysts:

As in adsorption, catalytic reactions take place within the cavities of crystalline zeolites. The zeolites important in catalysis are those which have the largest pore sizes and maximun available void volume. Since zeolites of this type are either rare or nonexistent in nature, molecular sieve catalysts are based on synthetic zeolites. Sieving effect may occur in catalysis, just as in adsorption. If a zeolite is to be used as a catalyst, the pore size of the zeolite should be such that the reactants can permeate the zeolite structure and the products can exit out of it.

Synthetic Zeolites:

Although certain naturally occuring zeolite minerals have been utilized to a limited extent, synthetic zeolites are better suited to meet the stringent requirements imposed on the molecular sieve adsorbents in adsorption and catalytic processes. For the use of molecular sieves in adsorption and catalysis they should meet closely controlled specifications in terms of purity, mechanical properties and porosity. A comparison of the important aspects of zeolite minerals and synthetic zeolites, (Table 1.1) considered in major applications as molecular sieves clearly brings out the advantages of the synthetic zeolites.

TABLE 1.1: COMPARISON OF NATURAL ZEOLITES VS

SYNTHETIC ZEOLITES (Breck, 1975)

Property	Natural zeolites	Synthetic zeolites
Availability	Restricted to occurrence as 8 or 9 species	Many types are available by manufacture from inexpensive raw materials.
Purity	Generally improve. Bedded deposits are mixtures, cation contents are complex. Undesirable impurities such as iron are common.	Manufactured as pure species. Other cationic forms are prepared by cation exchange.
Pore size	Limited	Available from $3\overset{\circ}{A}$ upto $8\overset{\circ}{A}$
Pore volume	Limited. Only chabazite and erionite have good pore volume	Upto 50 per cent by volume
Catalytic activity	Limited due to small pore sizes and impurities	Wide applicability

Various zeolites have been synthesized by earlier workers from gels prepared using inorganic chemicals like sodium silicate and silica gel and clays like metakaolin and also glasses as sources of silica (Breck,1974). For the first time, mordenite type zeolite has been successfully synthesized by Bajpai (1977) using silica from rice husk ash. Rice husk ash, after it is burnt to be carbon free contains nearly 90 per cent silica which is more reactive than the conventional silica sources like sodium silicate and silica gel.

As reviewed in the subsequent chapter zeolite Y, which has a wide range of applications both as an adsorbent and as a catalyst, has been synthesized by earlier workers from sodium silicate, silica gel and metakaolin (Breck and Flanigen, 1958 1968; Breck, 1964; Howell & Acara, 1964; Howell, 1968). In the present investigations, the following aspects have been attempted:

1. Feasibility of utilizing rice husk ash as a silica source for the synthesis of zeolite 'Y' type.

2. To study of the effect of various compositional parameters namely Na_2O , Al_2O_3, SiO_2 and water in the starting mix as also the effect of temperature and time of crystallization on the synthesis of zeolite Y from the $Na_2O-Al_2O_3-SiO_2-H_2O$ system

3. Investigations on the coexistance and stability

relations for the two zeolite species Y and P since these two species crystallize together within the range of composition, temperature and time chosen in the current studies.

CHAPTER 2

EXISTING LITERATURE

Structure of Zeolite Y:

Typical oxide formula of zeolite Y is $Na_2O.Al_2O_3.$
$4.8SiO_2.8.9 H_2O$. Zeolite Y is structurally related to
the mineral faujasite and hence it is referred to as
"faujasite-type". In its structure, truncated octahedra
exists as primary building units with the double O-rings as
the secondary building units. A truncated octahedron has
36 edges, 6 square faces 8 hexagonal faces and 24 vertices
with a tetrahedral atom (Al,Si) located at each of the
vertices. Oxygen atoms are located between the tetrahedral
atoms but not necessarily on the edge. The edges are not
meant to portray bonds, but merely the geometry of the
polyhedron (Figure 2.1). A double 6-ring is shown in the
Figure 2.2. Only the positions of tetrahedral silicons and
aluminums are shown. Oxygen atoms lie near the connecting
solid lines which are not intended to mean bonds.

The framework consists of a diamond - like array of
linked octahedra which are joined tetrahedrally by the
hexagonal faces through the double 6-rings (Figure 2.3).
The linkage between adjoining truncated octahedra is a
double 6-ring or hexagonal prism, containing 12 $(Si,Al)O_4$
tetrahedra. This results in wide cavities of nearly spherical
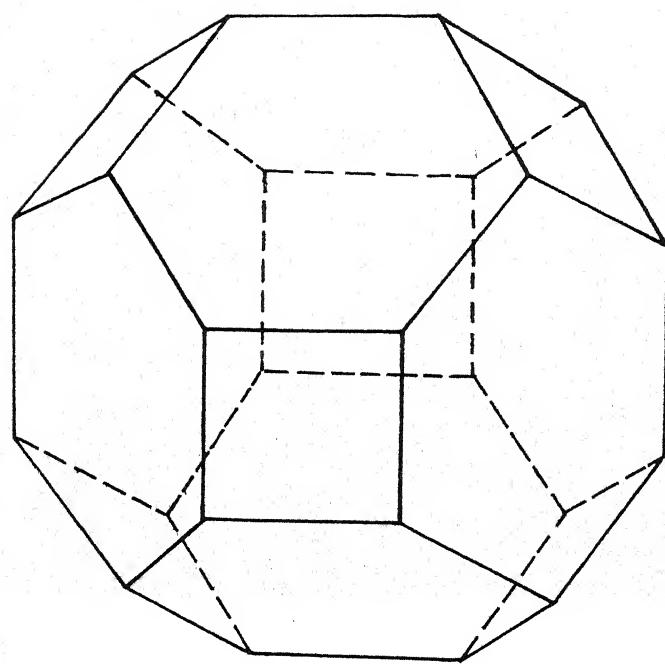
Fig. 2·1 – The truncated octahedron primary
building unit in the structure of
zeolite Y.
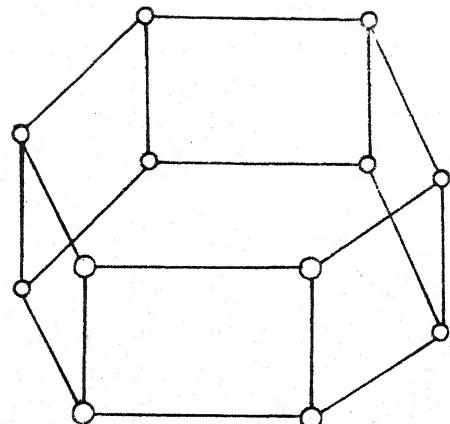
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Fig. 2·2 -Secondary building unit in the structure of zeolite Y. (Meier,1968).
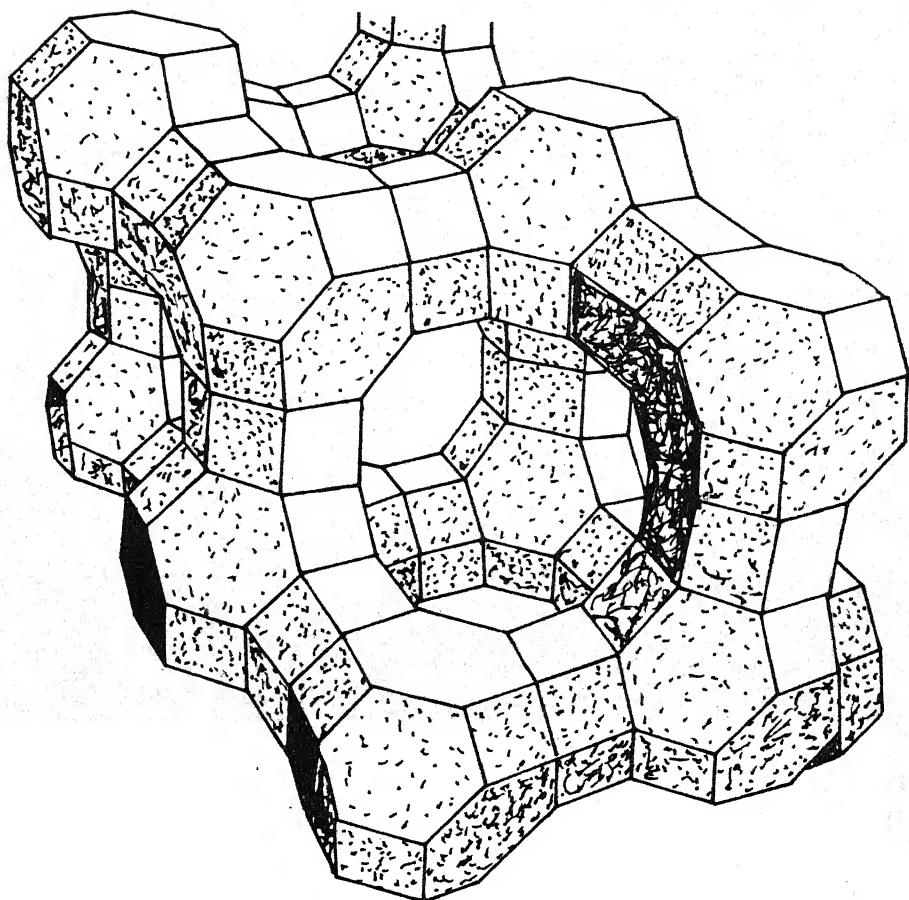
Fig. 2·3 – Line drawing for the structure of zeolite Y.

shape , each of which opens by common windows into four, identical, tetrahedrally distributed cavities. (Broussard and Shomaker, 1960; Barrer, Bultitude and Sutherland 1957).

Structure of Zeolite P:

A series of synthetic zeolites referred to as phillipsite-like, harmotome-like and gismondine-like exhibiting subtle differences are termed as P zeolites (Barrer, Bultitude and Kerr, 1959; Barrer, Baynham, Bultitude and Meier, 1959). Structurally two common types are recognized namely the cubic variety (P_c) and the tetragonal variety (P_t). Baerlocher and Meier (1972) showed the frame work structure of zeolite P to be the same as that of gismondine. Barrer, Bultitude and Kerr (1959) studied the adsorption of ammonia on Na,Ca and Ba forms of zeolite P.

Synthesis:

Having considered the advantages of synthetic zeolites over natural ones in the earlier chapter the methods of zeolite synthesis and the important factors in the synthesis and crystallization are considered here.

Simplexity Principle

The crystallization of zeolites is consistent with the simplexity principle proposed by Goldsmith (1953)

which relates the ease of crystallization to structural "simplexity". Goldsmith defines high simplexity as being "synonomous with disorder structural simplicity, or high entropy". The disordered form of an alumino silicate is in a state of high simplexity than its ordered counterpart.

The growth of crystalline aluminosilicates such as zeolites first requires the formation of a nucelus. In a system with high disorder, the principle favours the formation and development of a nucelus with high simplexity, which may be the nucleus of a crystal of a metastable phase.

Zeolite Metastability:

Many of the synthetic zeolites which do not have mineral relatives are non-equilibrium phases and do not exist when true equilibrium, conditions prevail. Many of the known synthetic zeolites are not structurally related to a mineral. This may be due to the metastability of the synthetic zeolite and its ease of conversion to a more stable species.

The crystallization of zeolites from reactive gels can be discussed in terms of free energy relations (Fig. 2.4). The initial reaction mixture is composed of components which first form phase 'a', which may convert to phase 'b' or 'c' with time. In the region where the temperature is such that 'a' or 'b' can both form, the nucleation and growth rates are important; the metastable phase 'a' which preferentia
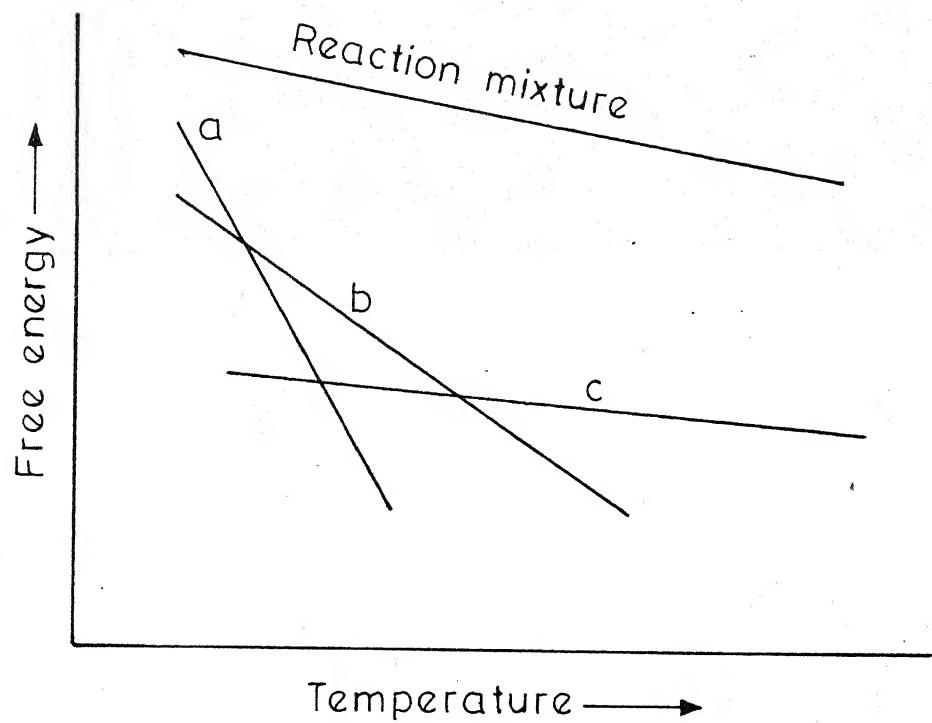
Fig. 2·4 – Schematic free energy relations between reaction
mixtures and various zeolile phases, represented
by a, b, c. (Fyfe, 1960).

forms may transform to the more stable phase b and in succession to c (Fyfe, 1960).

Some General Conditions for Synthesis:

The conditions generally used in synthesis are (Breck and Flanigen, 1960; Barrer, 1968):

1. Reactive starting materials such as freshly coprecipitated gels, or amorphous solids.

2. Relatively high pH introduced in the form of an alkali metal hydroxide or other strong base.

3. Low temperature hydrothermal conditions with concurrent low autogeneous pressure at saturated water vapor pressure.

4. A high degree of the supersaturation of the components of the gel leading to the nucleation of a large number of crystals.

The gels are crystallized in a closed hydrothermal system at temperatures varying generally from room temperature to about 175°C. In some cases higher temperatures to 300°C are used. The pressure is generally the autogenous pressure approximately equivalent to the saturated vapor pressure (SVP) of water at the temperature designated. The time required for crystallization varies from a few hours to several days.

For the $Na_2O \cdot Al_2O_3 \cdot SiO_2 \cdot H_2O$ system, the gel preparation and crystallization is represented schematically as follows:

$$NaOH \text{ (aq)} + Na \; Al(OH)_4 + Na_2 \; SiO_3 \text{ (aq)}$$

$$\downarrow \quad T_1 = 25°C$$

$$Na_a(AlO_2)_b \; (SiO_2)_c \; NaOH \; H_2O \quad gel$$

$$\downarrow \quad T_2 = 25 \text{ to } 175°C$$

$$Na_x \Big[(AlO_2)_x \; (SiO_2)_y \Big] \; m \; H_2O + solution$$
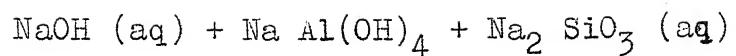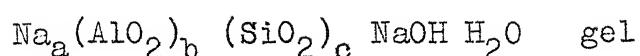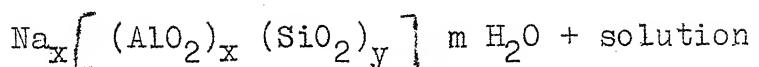
zeolite crystals.

Synthesis of Zeolites Y and P:

Both zeolite Y and zeolite P were synthesized from chemical silica like sodium silicate and clays like metakaolin.

Zeolite Y was synthesized (Breck, 1964; Breck and Flanigen, 1968) using sodium aluminate, sodium silicate, sodium hydroxide and colloidal silica as the reactants. Typical reactant composition was Na_2O/Al_2O_3: 8, SiO_1/Al_2O_3:20 and H_2O/Al_2O_3 :320 (mole ratios). The temperature of the reactor was between 20 and 175°C. Zeolite Y crystallized had the composition Na_2O/Al_2O_3: 1, SiO_2/Al_2O_3: 3-6 and H_2O/Al_2O_3: 9 (mole ratios).

Howell and Acara (1964) synthesized zeolite Y using metakaolin, NaOH, sodium silicate and NaCl ($NaCl/Al_2O_3$ = 2) as the reactants. The reactant composition was Na_2O/Al_2O_3:3.5 SiO_2/Al_2O_3:7 and H_2O/Al_2O_3: 140 (mole ratios). The gel was aged at room temperature for 24 hours and the reaction was carried out for 24 hours at a temperature of 100°C.

Zeolite Y crystallized had the composition Na_2O/Al_2O_3: 1.0 and SiO_2/Al_2O_3 : 3.5. Howell (1968) synthesized zeolite Y using calcined, acid - leached metakaolin and NaOH as the reactants. The reactant composition was Na_2O/Al_2O_3:5, SiO_2/Al_2O_3: 10 and $H_2O:Al_2O_3$: 200 (mole ratios). The gel was aged at room temperature for 24 hours and the reaction was carried out for 72 hours at 100°C. Zeolite Y crystallized had the composition Na_2O/Al_2O_3:1 and SiO_2/Al_2O_3:4.1.

Zeolite P_c was synthesized (Pereyron, Guth and Wey, 1971; Milton, 1961) using $NaAlO_2$, sodium silicate, NaOH and colloidal SiO_2 as the reactants. Typical reactant composition was Na_2O/Al_2O_3: 2, SiO_2/Al_2O_3:3.8 and H_2O/Al_2O_3: 94 (mole ratios). The temperature was varied from 60 to 150°C. Zeolite P_c crystallized had the composition Na_2O/Al_2O_3:1, SiO_2/Al_2O_3: 2-5 and H_2O/Al_2O_3:5. Taylor and Roy (1964) synthesized zeolite P_t using $NaAlO_2$, sodium silicate, NaOH and colloidal SiO_2 as the reactants. Typical reactant composition was Na_2O/Al_2O_3:6, SiO_2/Al_2O_3:8 and $H_2O/solids$:6 The temperature was varied from 60 to 250°C Zeolite P_t crystallized had the composition Na_2O/Al_2O_3:1, SiO_2/Al_2O_3: 3.2-5.3 and H_2O/Al_2O_3 around 5.

For the synthesis of zeolite Y it is observed that the composition ranges within the limits given in Table 2.1.

TABLE 2.1 SOME COMPOSITIONS FOR SYNTHESIS OF ZEOLITE Y
(Breck, 1964)

Molar ratio	Non-aged	Aged
Na_2O/SiO_2	0.4 to 0.6	0.28 - 0.30
SiO_2/Al_2O_3	15 to 25	8-10
H_2O/Na_2O	20 to 50	30 -50

If the reaction mixture is first digested or aged at room temperature and then subsequently heated at the higher temperature usually 100°C, the Si/Al ratio in the synthetic Y is higher as shown in Table 2.2. Room temperature aging reduces the SiO_2/Al_2O_3 ratio in the gel necessary to form zeolite Y.

TABLE 2.2: SYNTHESIS OF ZEOLITE Y FROM AGED GELS
(Breck, 1964)

Typical $\dfrac{Na_2O}{SiO_2}$	Reactant $\dfrac{SiO_2}{Al_2O_3}$	Composition $\dfrac{H_2O}{Na_2O}$	Aging time (hr)	Crystallization Time at 100°C (hr)	Product Purity %	Si/Al
0.4	20	40	0	72	63	< 2.5
0.4	20	40	24	50	92	2.5
0.4	10	40	24	50	92	2.5
0.3	8	40	24	96-144	100	2.6
0.3	10	40	24	96-144	95	2.8

The activity of silica during crystallization of zeolites of variable silica content was emphasized by Coombs et al.(1959). The use of a more reactive amorphous silica is

important in the synthesis of high silica zeolites like
zeolite Y.

Breck and Flanigen (1968) observed that when
colloidal silica was used to prepare the gel for crystalli-
zation of sodium zeolites at 100°C zeolite Y was formed
from gel compositions, which in the soluble silicate system
might result in the formation of zeolite P.

Certain ions which form stable complexes with
aluminium in solution in particular phosphate, have been
used to modify the usual composition of the zeolite as it is
influenced by the composition of the initial gel. A more
efficient use of the silica in the crystallization of zeolite
Y was reported when phosphate was present in the gel.
Phosphate has been used in the aluminosilicate gel to control
aluminum substitution and the Si/Al ratio in the synthesis of
zeolite Y (Kuhl, 1967 and 1971).

Zeolite P is stable at higher temperatures and
has been formed over a temperature range of 60-200°C. In
general, at 200°C and SVP, the zeolite P, analcime and
hydroxysodalite are the dominant stable phases. Zeolite P
appears to be an equilibrium phase. Several structurally
related types have been synthesized including a cubic and
a tetragonal form. The synthetic P zeolites dominate the
synthesis composition fields in the low temperature range
of 100-150°C (Milton, 1961). Several types of zeolite P have
been identified (Beard, 1971).

Zeolite P, which forms readily as the equilibrium phase at elevated temperatures does not crystallize readily at lower temperatures. At ambient temperature the composition field is dominated by zeolite Y, A and X. Above 150°C, zeolite P is the dominant phase along with zeolite A and analcime. At high Na_2O concentrations, the synthetic hydroxysodalite is formed. This is in accordance with the principle discussed earlier relative to the free energy-temperature relationship for metastable phases. At low temperature, the more complex and more easily nucleated zeolite Y or X are formed, whereas the increasing temperature of crystallization favours the formation of zeolite P followed ultimately by analcime. As shown schematically in figure 2.1, zeolite Y corresponds to phase a, zeolite P would correspond to phase b and analcime to phase c. The free energy curves for b and c would intersect at about 175°C and for a and b at about 100°C. This is consistent with the interesting behaviour of the reacting phases during nucleation; for example zeolites Y and P may form in the same overall composition field, but the type of reactant silica seems to control which species nucleates (Breck, 1974).

Applications of Zeolite Y:

Zeolite Y with its most open structure (void volume 0.48 cc/cc and dehydrated free apertures 7.4 Å) and with

its high Si/Al ratio of 1.5 to 3.0 has got a wide variety of applications.

Ortho-para Hydrogen Conversion:

Ortho-para hydrogen conversion was studied at -196°C on sodium Y-zeolites by Turkevich and Ciborowski (1967). Hydrogenation: Breck (1961) discloses in a U.S. patent the use of zeolite Y loaded with metallic zinc or zinc oxide for the purpose of obtaining a catalyst for the synthesis of methanol.

Cracking:

Peguzova and Vatukhina (1963 and 1964) studied the cracking of kerosine gas oil fraction on H and Y forms of zeolite Y and showed that they yield twice to what CaX does.

Topchieva et al. (1965) studied the cracking of cumene on a series of zeolites and found that the energy of activation for zeolite Y was much lower than that of zeolite X.

Hydrocracking:

The hydrocracking of n-dodecane over platinum on CaY is studied by Schulz and Weitkamp (1972 and 1973). The hydrocracking of n-hexane and cyclohexane over palladium containing HY was studied by Voortices and Hatchen (1969)

Dehydration:

Minachev and coworkers (1963) investigated the dehydration of alcohols on CaY zeolite (Si/Al = 1.7) and found that at 250°C all the primary alcohols dehydrated smoothly into the olefins

Oxidation:

A.U.S. Patent (1961) discloses the possibility of using zeolite Y for the oxidation of organic compounds, and in particular for the oxidation of ethylene to ethylene oxide.

Isomerization:

Rabo and his associates reported on the (1961) isomerization of n-hexane and n-pehtane on Y zeolites. Minachev and coworkers (1963) studied the isomerization of n-pentane, n-hexane, n-heptane and cyclohexane on Pd, Pt Rh and Ir catalysts supported on zeolite Y and the hydrogenation and hydroisomerization of benzene on Rh, Ir and Pd supported on CaY. Lombardo and Velez (1973) studied the kinetics and mechanism of isomerization of n-butene and n-pentene over Na-Y zeolites.

Alkylation:

Minachev and coworkers (1963) alkylated benzene with ethylene over NaY and CaY zeolites of which the Ca form was more effective. Mays and Pickert (1967) report that high activity for alkylation of aromatic hydrocarbons with C_2-C_{12} olefins or alkyl halides can be obtained at low temperatures and pressures using catalyst prepared from multivalent cation-exchanged or decationated Y type zeolites. Nolley and Katzer (1973) report on benzene alkylation with olefins over Y zeolites. Alkylation of isobutane using rare earth Y catalysts was reported by Kirsh and Potts (1971). Yang worked on the

alkylation of isobutane with ethylene using zeolite Y catalyst.

Hatakada, Ono and Keii (1973) studied the reactions of aromatic compounds with ammonia over Y zeolite.

CHAPTER 3

EXPERIMENTAL

Materials:

In the present investigation, rice husk ash, sodium hydroxide, aluminium hydroxide and silica gel were used as the materials in the starting mix for the synthesis of the zeolites under study.

Sodium hydroxide used was in the form of pellets (supplied by ARC Industries, Kanpur) is of 96.0 per cent purity. The aluminium hydroxide was obtained from APEX Chemicals, Bombay in the form of fine powder. The silica gel (of BDH make) is ground in a ball mill to (-200) mesh size.

Rice husk as obtained from a rice-mill in Utripura (situated around 40 kms from Kanpur city) was burnt in a muffle furnace at 1000°C for 6 hours to get carbon free ash. The ash thus obtained was ground in a ball mill to get particle size of (-200) mesh. X-ray diffraction pattern of the ash (Figure 4.1) indicated that the silica was in the form of α-cristobalite.

Apparatus:

The autoclave used in the synthesis is a high pressure reactor of Parr make (Series 4500). This unit consists of a

stainless steel vessel B.of one litre capacity, which
is designed to withstand 1000 psig pressure and 350°C
temperature (Figure 3.1). A motor driven stirrer S is
provided. A gas release valve V_1 is provided to release the
pressure in the autoclave at the end of a run Liquid
samples containing fine particles can be collected during
the run through the valve V_2. A dial thermometer is provided
to read the temperature of the gel.

The autoclave tightly fits into the heater assembly H
to which power is supplied through a 230V variac thus
controlling the temperature of the reaction mixture to an
accuracy of $\pm$ 2°C by the variac. The desired temperature
is attained within 30-40 minutes.

Method of Synthesis:

The silica solution was prepared by treating the
rice husk ash with 2-3 molar aq. NaOH solution at 80°C for
two hours with continuous shaking. Then the solution was
filtered under vacuum to separate the insolubles. Fine silica
gel is added to this solution if additional amount of silica
was desired.

The sodium aluminate solution was prepared by adding
aqueous NaOH solution to $Al(OH)_3$ powder and the solution
was heated to boiling.

The sodium silicate and aluminate solution were mixed
slowly with continuous shaking to give the sodium alumino-
silicate gel of desired composition.
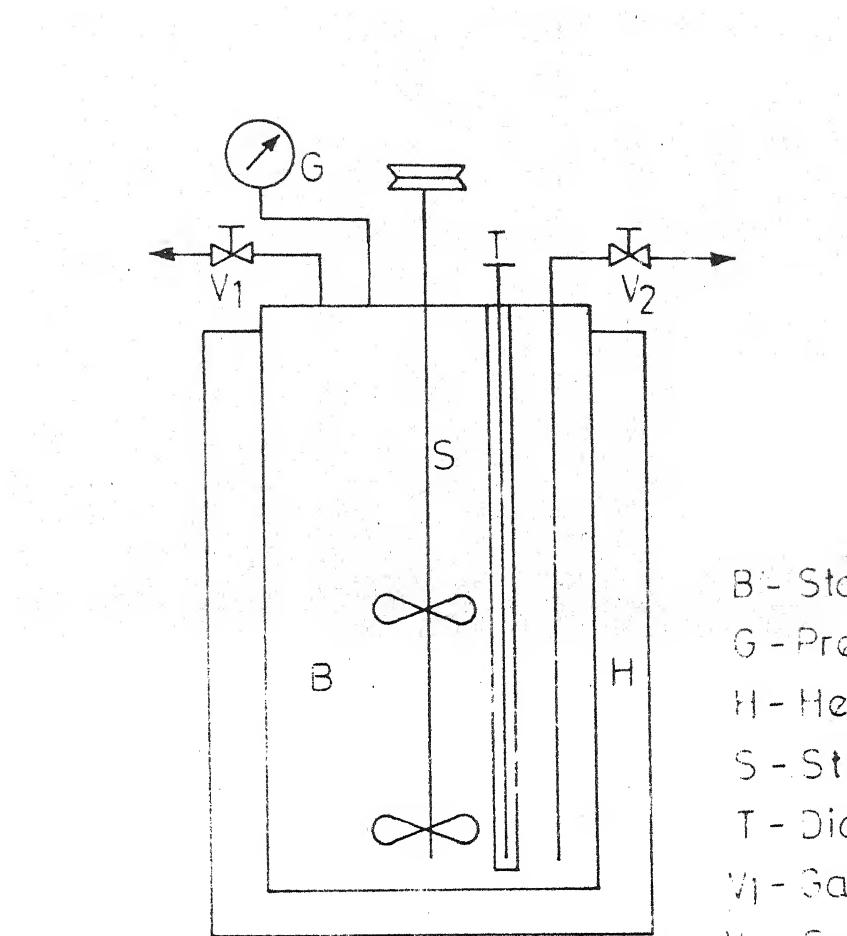
B - Stainless steel vessel
G - Pressure gauge
H - Heating assembly
S - Stirrer
T - Dial thermometer
V₁ - Gas release valve
V₂ - Sampling valve

Fig. 3.1 - Line diagram for the autoclave assembly.

This reaction mixture was charged in the autoclave for hydrothermal reaction and it was raised to the desired temperature. Liquid samples containing fine solids were taken at regular intervals of time while the reaction proceeded. These samples were filtered under vacuum and the solid samples were dried in an oven at 120°C for 12 hours.

In the synthesis the temperature of reaction is varied from 60 to 100°C. Samples were taken at different times between 12 hours and 72 hours of reaction time. In the starting gel Na_2O/Al_2O_3 molar ratio was varied from 4 to 9 and SiO_2/Al_2O_3 molar ratio was varied from 2 to 22. The water content of the gel was varied from 90 - 95 mole percent.

Characterization:

X-ray diffraction analyses were carried out for all samples on General Electric unit fitted with XRD-6 diffracto- meter using copper K_α radiation with nickel filter. Scanning was done in the range of 5-50° (2θ) at a rate of 2°/min with a chart speed of 1"/min. The interplanar spacings (d) were obtained using Bragg's equation.

CHAPTER 4

RESULTS AND DISCUSSION

In the present study, synthesis of the zeolites has been carried out in the system $Na_2O - Al_2O_3 - SiO_2-H_2O$ by varying the reaction temperature, the reaction time and the composition of the starting mixture within the chosen ranges. The ranges for these parameters are as follows:

Reaction temperature: 60 –100°C

Time: 12 – 72 hours

Composition of the starting mixture (in mole ratio)

Na_2O/Al_2O_3 = 4 – 9

SiO_2/Al_2O_3 = 2.5 – 22

H_2O/Al_2O_3 = 170 – 360

In the starting mixture 90-95 per cent (molar) water was maintained.

The main products appeared from time to time are zeolite Y, zeolite P_c, hydrated sodalite, and analcime. The products have been characterized with/ the x-ray diffraction technique and the area under the strongest peaks in x-ray diffraction pattern for each one of these zeolites is calculated and has been taken to represent the relative amount of its crystallization. Typical x-ray diffraction patterns for some of the runs are indicated in Figures 4.2 – 4.9.
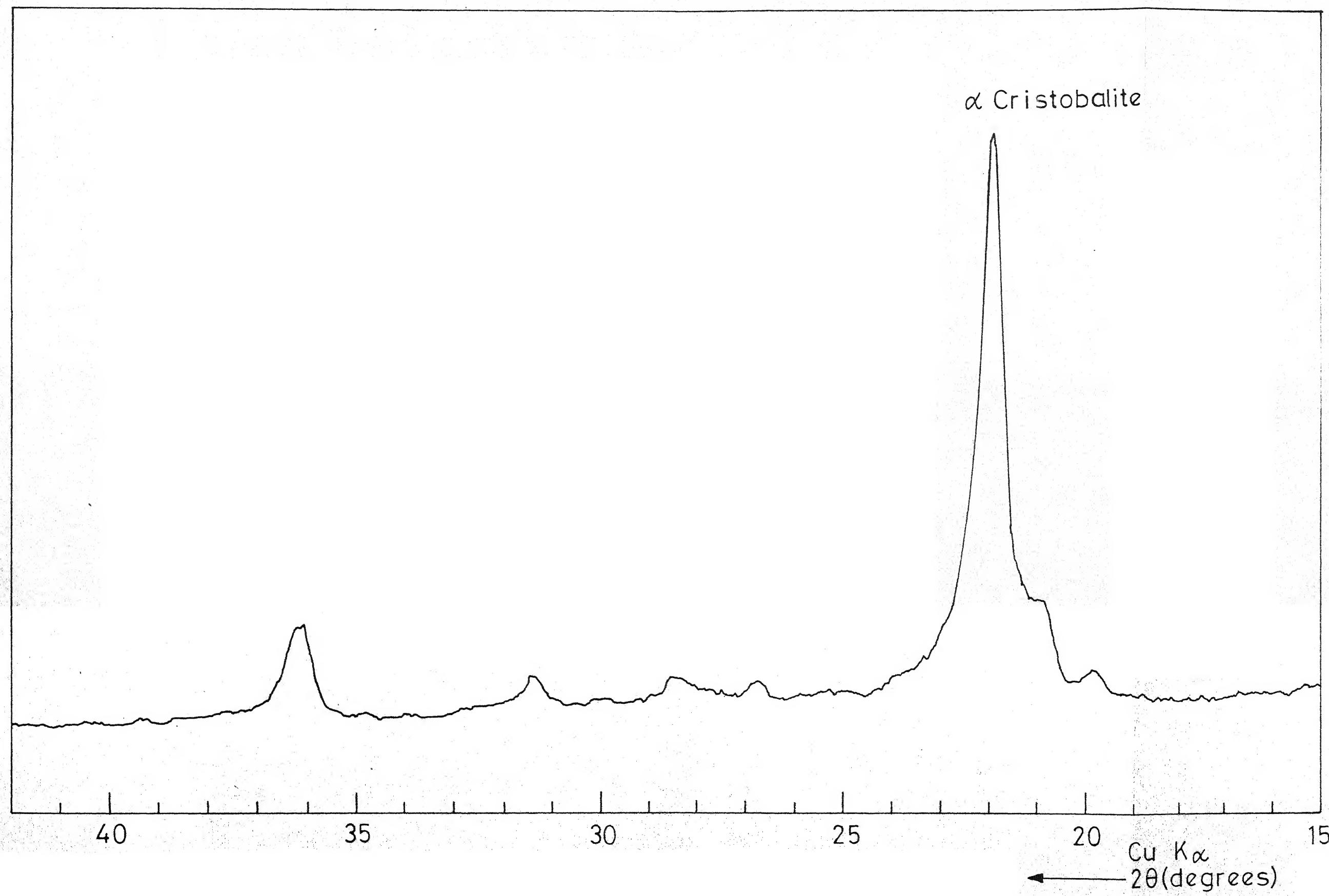
Fig. 4·1 – Typical X-ray diffraction pattern for rice husk ash burnt at 1000 °C.

Composition $= 7Na_2O : Al_2O_3 : 14SiO_2 : 260\ H_2O$

Temperature $= 70°C$

Time $= 24$ hrs.

Y $=$ Zeolite Y

$P_C =$ Zeolite P_C

Cu Kα

$\longleftarrow 2\theta$ (degrees)
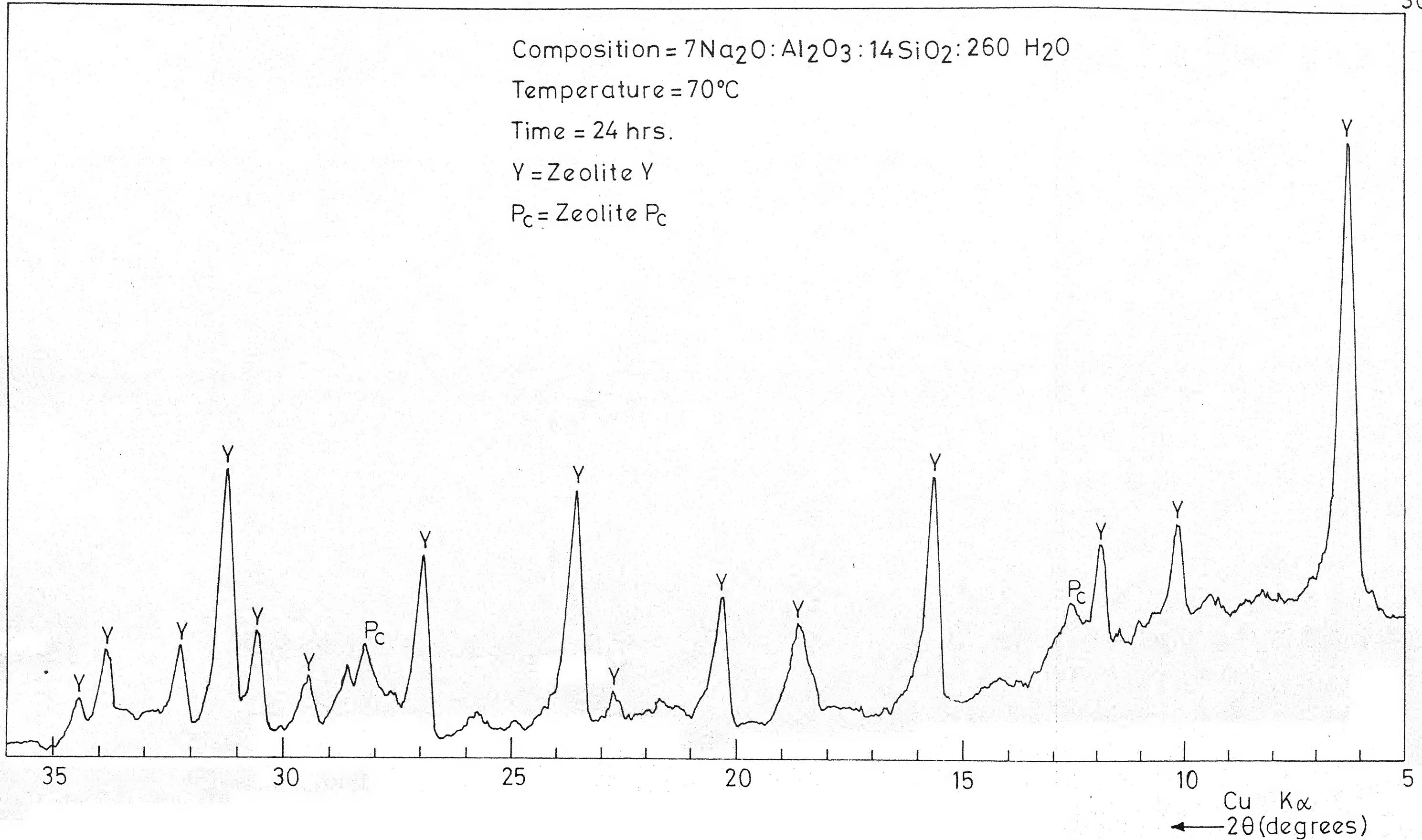
Fig. 4·2 – Typical X-ray diffraction pattern for run no. 913.

Composition = $7Na_2O:Al_2O_3:14SiO_2:260H_2O$

Temperature = 70 °C

Time = 36 hrs.

Y = Zeolite Y

P_C = Zeolite P_C

Am = Analcime

Cu K_α

$\longleftarrow 2\theta$(degrees)
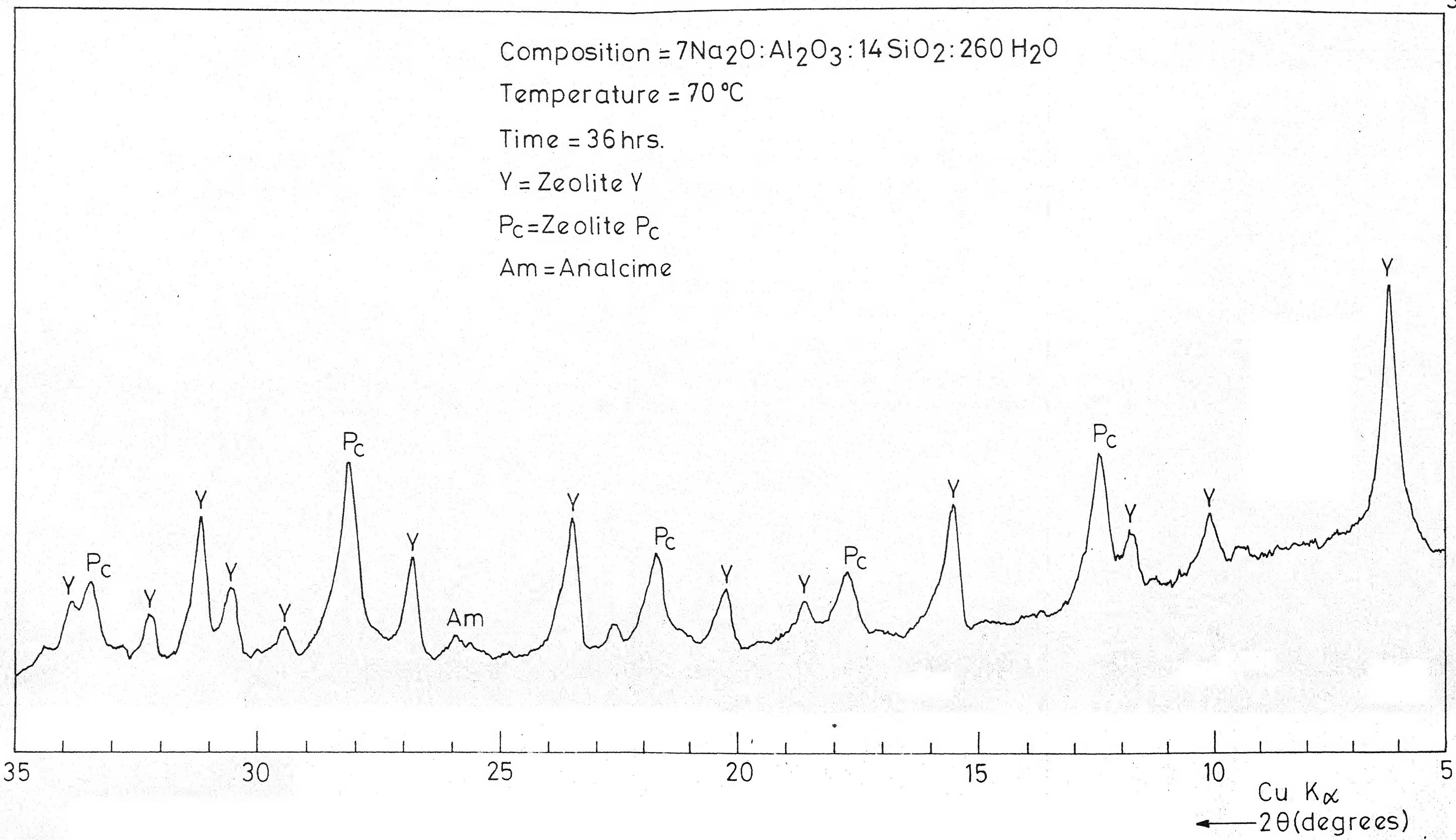
Fig. 4.3 – Typical X-ray diffraction pattern for run no. 914.

Composition = $7Na_2O : Al_2O_3 : 14SiO_2 : 260H_2O$

Temperature = 80 °C

Time = 36 hrs

Y = Zeolite Y

P_C = Zeolite P_C

Am = Analcime

Cu $K\alpha$

← 2θ (degrees)
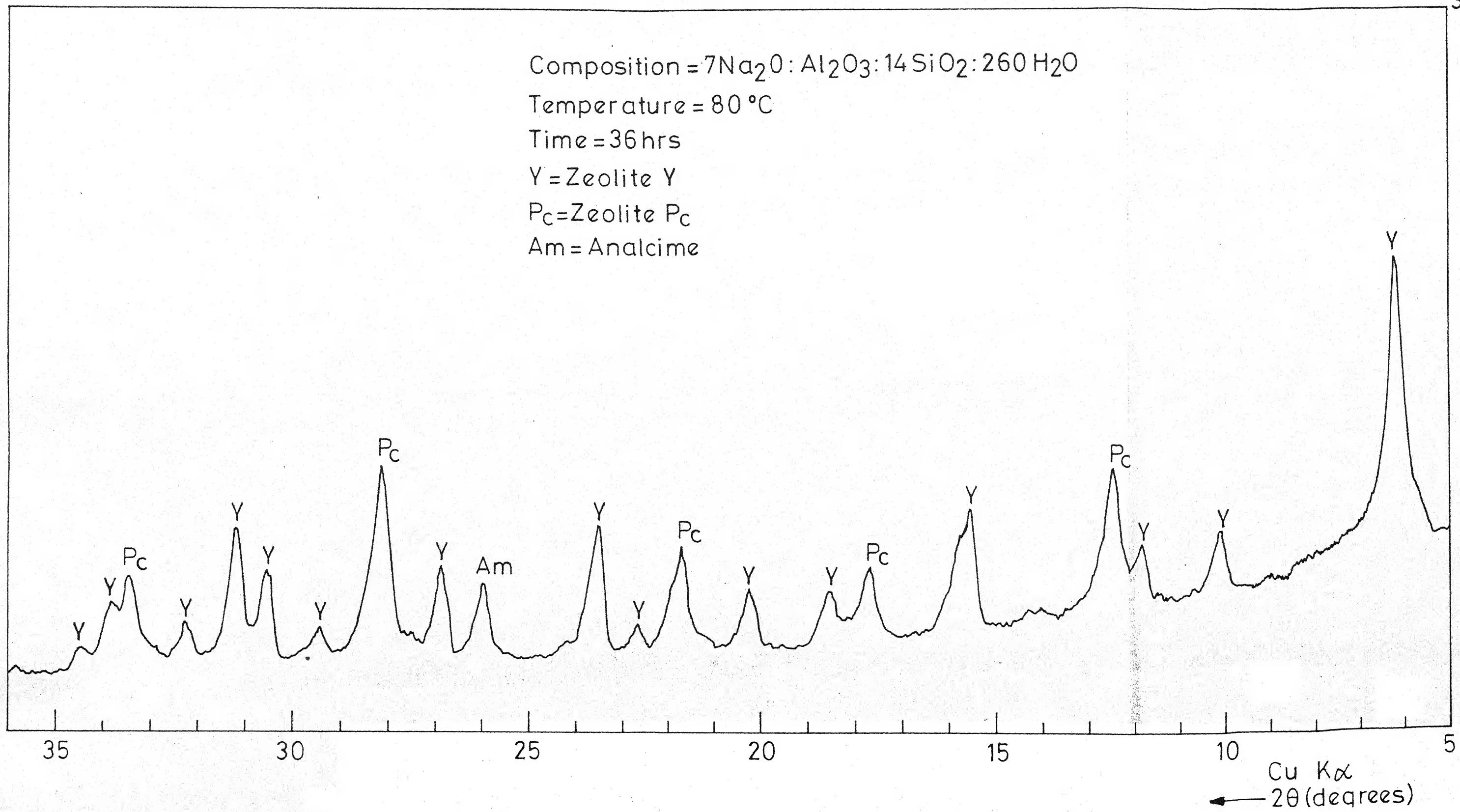
Fig. 4.4 – Typical X-ray diffraction pattern for run no. 924.

Composition = $6Na_2O$: : O_2 : $22 H_2O$
Temperature = 70°C
Time = 24 hrs.
Y = Zeolite Y
P_C = Zeolite P_C

Fig. 4·5 – Typical X-ray diffraction pattern for run no. 1012

Cu $K\alpha$
— 2θ(degrees)

Composition = $7 Na_2O : Al_2O_3 : 12 SiO_2 : 240 H_2O$

Temperature = 70 °C

Time = 24 hrs.

Y = Zeolite Y

P_C = Zeolite P_C

Am = Analcime

Cu K_α

← 2θ (degrees)
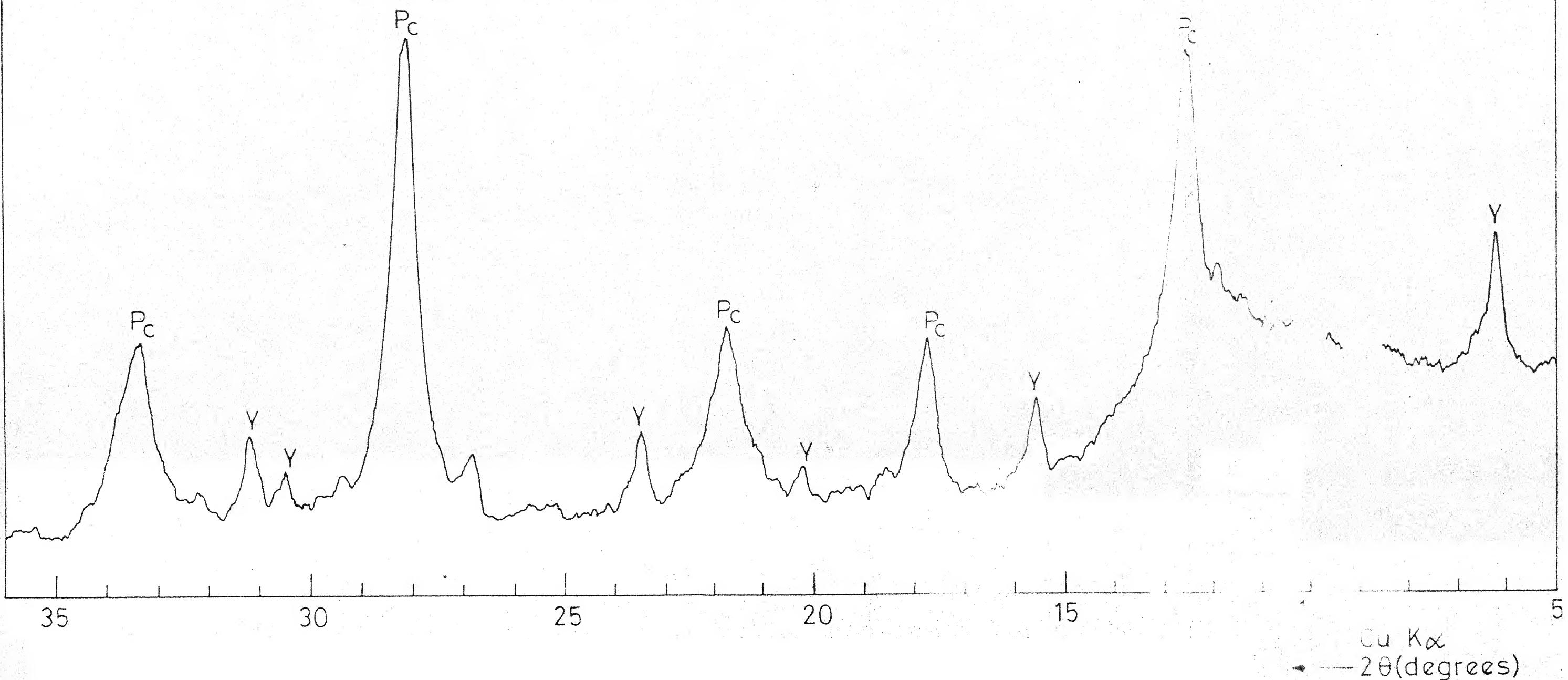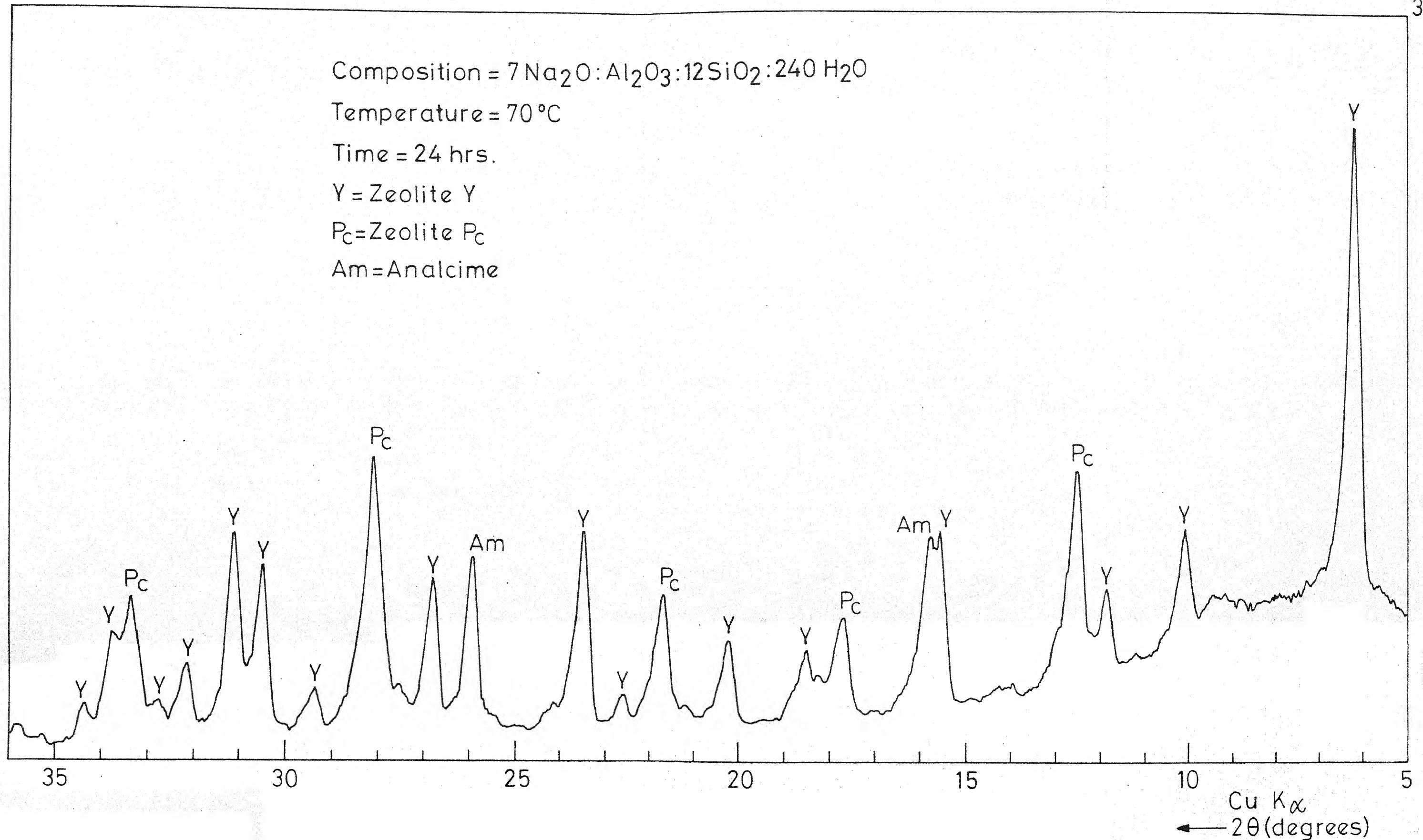
Fig. 4.6 – Typical X-ray diffraction pattern for run no. 1112.
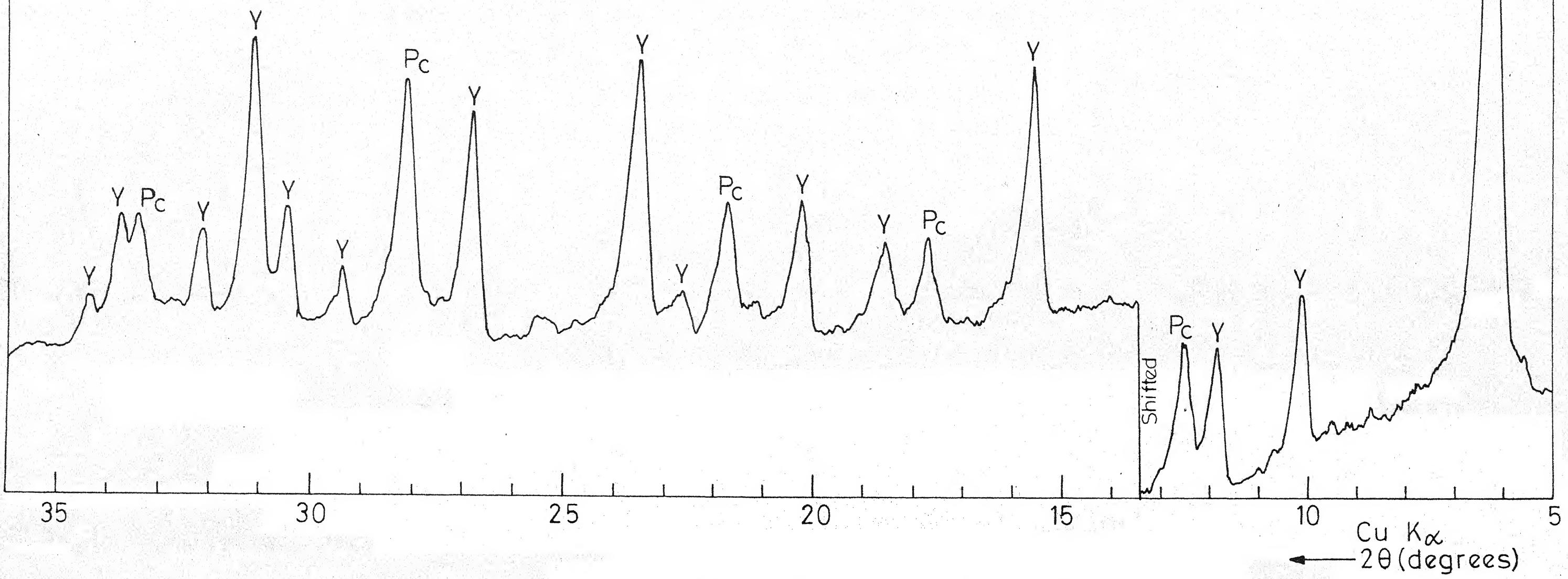
Fig. 4.7 – Typical X-ray diffraction pattern for run no. 1211.
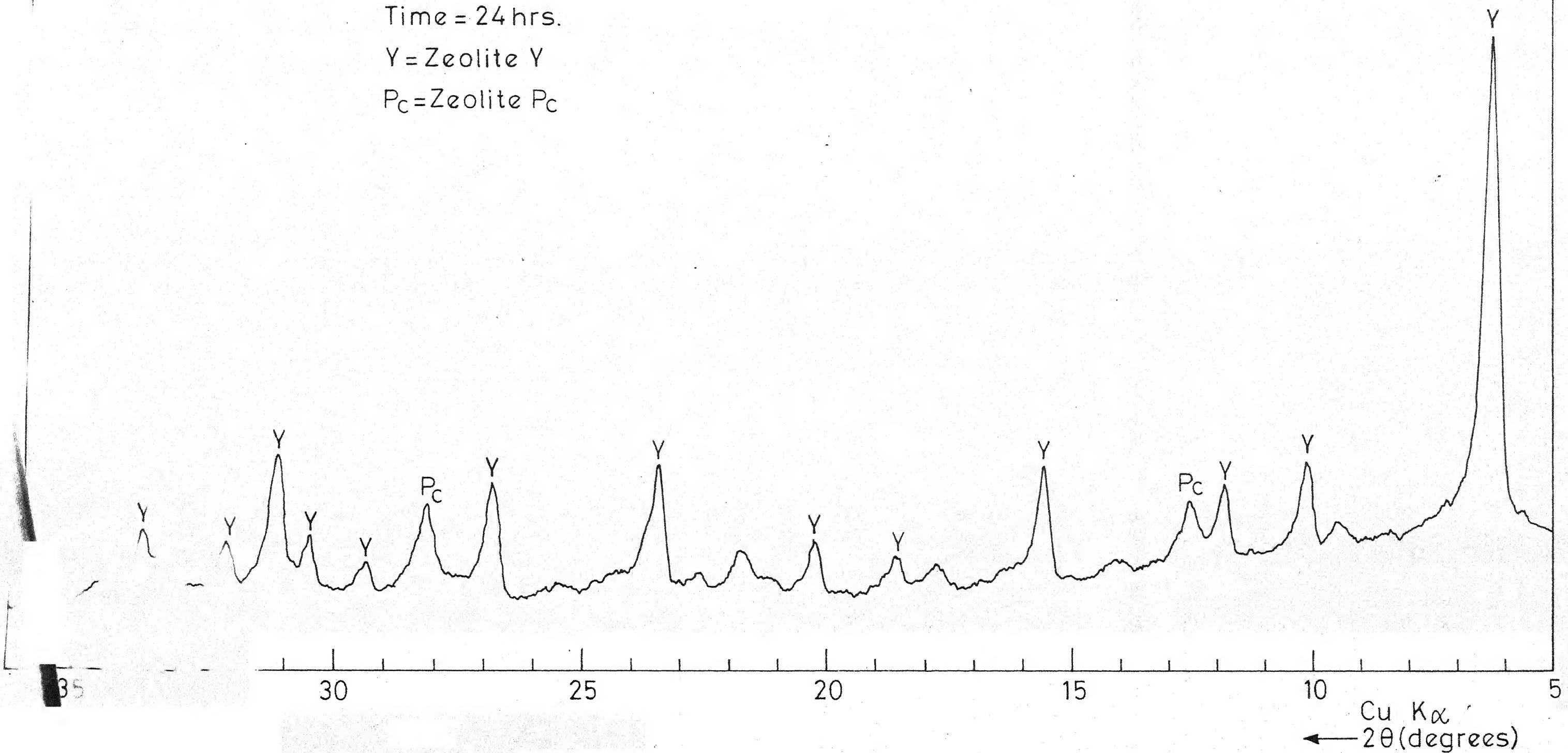
Fig. 4·8 – Typical X-ray diffraction pattern for run no. 1613.

Composition $= 7Na_2O : 5SiO_2 : 200H_2O : 1Al_2O_3$

Temperature $= 70\,°C$

Time $= 30$ hrs.

HS $=$ Hydrated sodalite
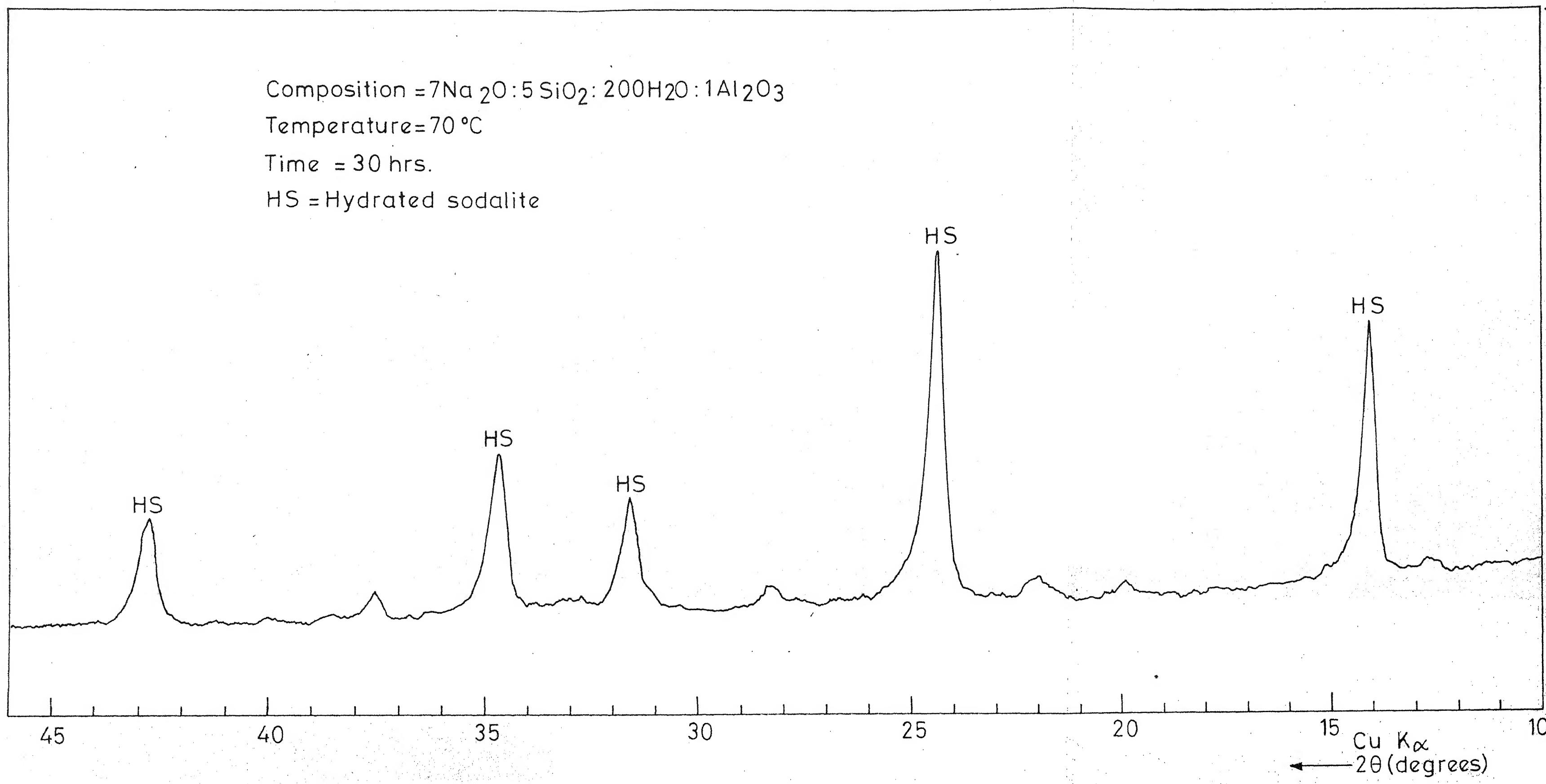
Fig. 4·9 — Typical X-ray diffraction pattern for run no. 1713.

The present investigations were confined to the temperature range 60 - 100°C since zeolites Y and P_c have been reported by earlier workers to appear within this range. A total of 200 runs have been conducted. The effect of various parameters has been brought out in rectangular coordinate plots presented in Figures 4.10 and 4.11.

Synthesis at 60 and 65°C

The x-ray diffraction patterns for the products obtained at 60°C and 65°C indicated the absence of the characteristic peaks for any zeolite species. Hence it can be inferred that no zeolite has been formed and the constituents in the mixture are amorphous at this stage. Even after 72 hours of reaction, no change has been found in the status of the reaction material.

Synthesis at 70°C

Results of typical runs conducted at 70°C temperature are presented in Table 4.1. The relative extent of crystallization of zeolites Y and P have been expressed in terms of ratio of the intensity of the strongest peak of zeolite Y to the intensity of the strongest peak of the zeolite P_c (i.e. $\frac{I_y\ 111}{I_{P_c}\ 310}$). As can be seen from the Table 4.2 at this temperature with Na_2O/Al_2O_3 ratios 4-7 and with only soluble silica from rice husk ash as the silica source zeolite HS is

TABLE 4.1: RESULTS OF TYPICAL RUNS:TEMPERATURE 70°C

Run No.	Reactant Composition (moles/Al_2O_3)			Time, hrs.	Intensity				
	Na_2O	SiO_2	H_2O		Y (111)	P_c (310)	An (400)	HS (211)	$\frac{Y(111)}{P_c(310)}$
1	2	3	4	5	6	7	8	9	10
111	4.0	2.5	180	8	—	—	—	—	—
113	4.0	2.5	180	24	—	—	—	9.0	—
114	4.0	2.5	180	48	—	—	—	5.0	—
311	4.5	3.0	170	24	—	—	—	16.0	—
411	5.0	4.0	180	24	—	—	—	21.0	—
511	8.0	20.0	320	12	—	—	—	—	—
512	8.0	20.0	320	24	1.3	5.5	—	—	0.24
513	8.0	20.0	320	48	0.1	6.0	0.1	—	0.)17
612	9.0	22.0	360	24	0.1	7.4	—	—	0.013
613	9.0	22.0	360	48	0.2	10.3	0.4	—	0.020
614	9.0	22.0	360	72	—	1.5	0.6	—	—
711	7.0	18.0	315	24	0.4	0.1	0.1	—	40.0
712	7.0	18.0	315	48	1.5	0.6	—	—	2.5
713	7.0	18.0	315	60	5.5	1.5	0.5	—	3.6
714	7.0	18.0	315	72	2.8	2.2	0.8	—	1.3
811	8.0	20.0	360	24	—	1.4	—	—	—
812	8.0	20.0	360	48	—	6.8	0.3	—	—
813	8.0	20.0	360	72	—	8.0	1.7	—	—
911	7.0	14.0	260	12	0.1	—	—	—	—
912	7.0	14.0	260	18	2.8	0.15	—	—	18.70

Table 4.1 (contd)

1	2	3	4	5	6	7	8	9	10
913	7.0	14.0	260	24	8.5	0.3	–	–	28 30
914	7.0	14.0	260	36	3.6	2.2	0.05	–	1.60
1011	6.0	12.0	220	18	1.3	12.5	–	–	0.10
1012	6.0	12.0	220	24	2.7	13.8	–	–	0.19
1013	6.0	12.0	220	36	1.0	14.5	–	–	0.07
1111	7.0	12.0	240	12	1.4	1.9	–	–	0.74
1112	7.0	12.0	240	24	9.8	4.5	2.2	–	2.18
1211	6.0	10.0	200	12	26.5	3.8	–	–	6.97
1212	6.0	10.0	200	24	18.0	3.9	–	–	4.61
1312	5.0	8.0	160	18	1.0	0.3	–	–	3.33
1313	5.0	8.0	160	24	4.0	5.2	0.05	–	0.77
1412	4.0	6.0	140	18	–	6.5	–	–	–
1413	4.0	6.0	140	24	1.0	20.0	–	–	0.05
1512	6.0	8.0	200	18	0.15	–	–	–	–
1513	6.0	8.0	200	24	1.6	1.9	–	–	0.84
1611	6.0	6.0	200	12	–	–	–	–	–
1612	6.0	6.0	200	18	9 8	0.3	–	–	32.67
1613	6.0	6.0	200	24	11.3	1.0	–	–	11.30
1713	7.0	5.0	200	30	–	0.1	–	10.0	–
1811	6.0	10.0	170	12	–	–	–	–	–
1812	6.0	10.0	170	18	–	–	–	–	–
1813	6.0	10.0	170	24	–	0.4	–	–	–

Table 4.1 (contd)

1	2	3	4	5	6	7	8	9	10
1911	6.0	8.0	150	12	0.6	0.08	–	–	7.50
1912	6.0	8.0	150	18	6.3	0.8	0.2	–	7.88
1913	6.0	8.0	150	24	6.5	1.0	0.3	–	6.5
2011	6.0	10.0	250	12	1.2	3.7	0.1	–	o.32
2012	6.0	10.0	250	18	0.3	8.8	–	–	o.03
2013	6.0	10.0	250	24	0.08	4.0	o.08	–	o.02

Temperature = 70°C
Time = 24 hrs
H_2O range 90-95%

$\dfrac{I\,Y\,(111)}{I\,P_C\,(310)} < 0.5$

$\dfrac{I\,Y\,(111)}{I\,P_C\,(310)} > 2$

$\dfrac{I\,Y\,(111)}{I\,P_C\,(310)} - 0.75\ \text{to}\ 1.0$

SiO_2/Al_2O_3

Na_2O/Al_2O_3
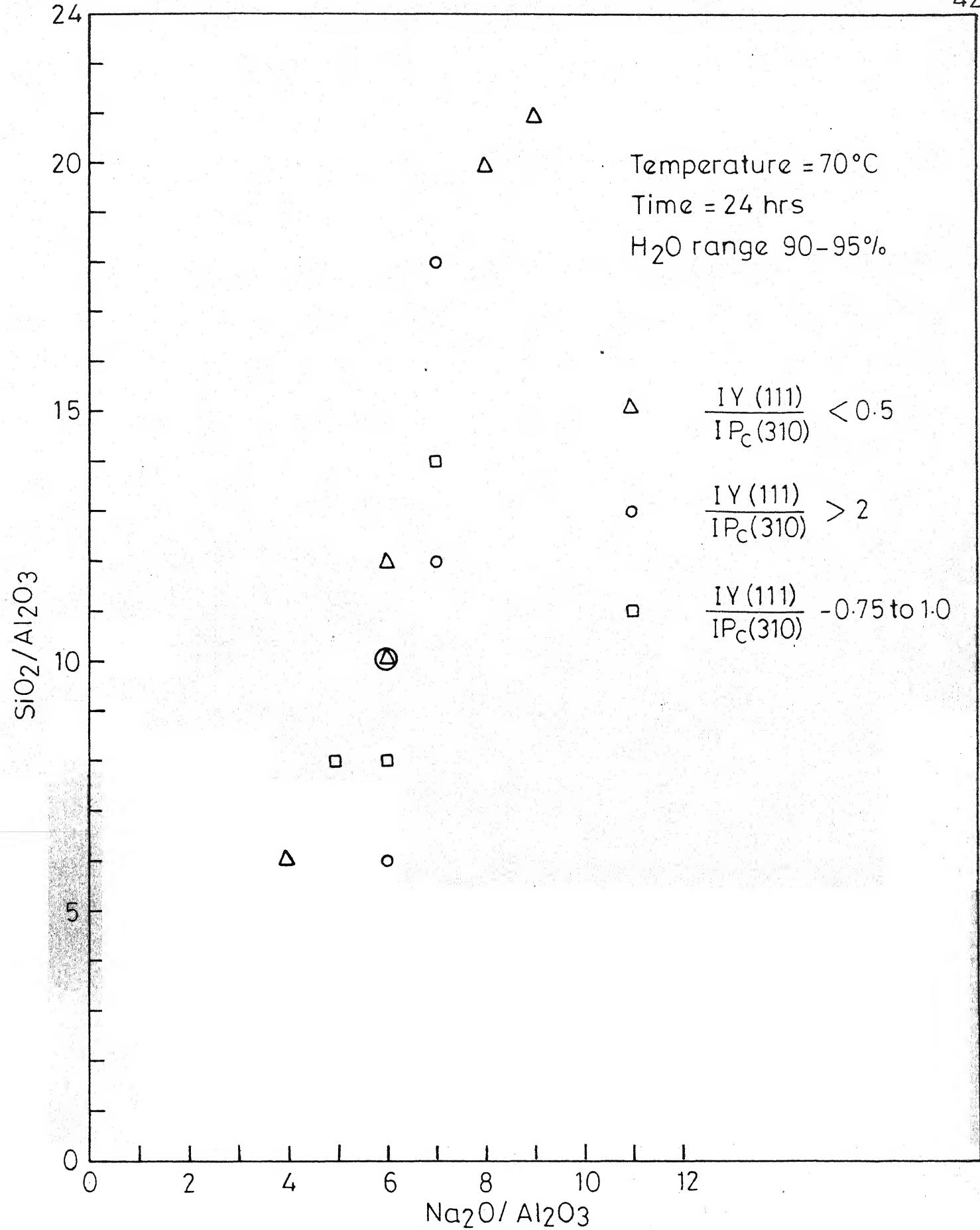
Fig. 4·10 - Effect of composition.
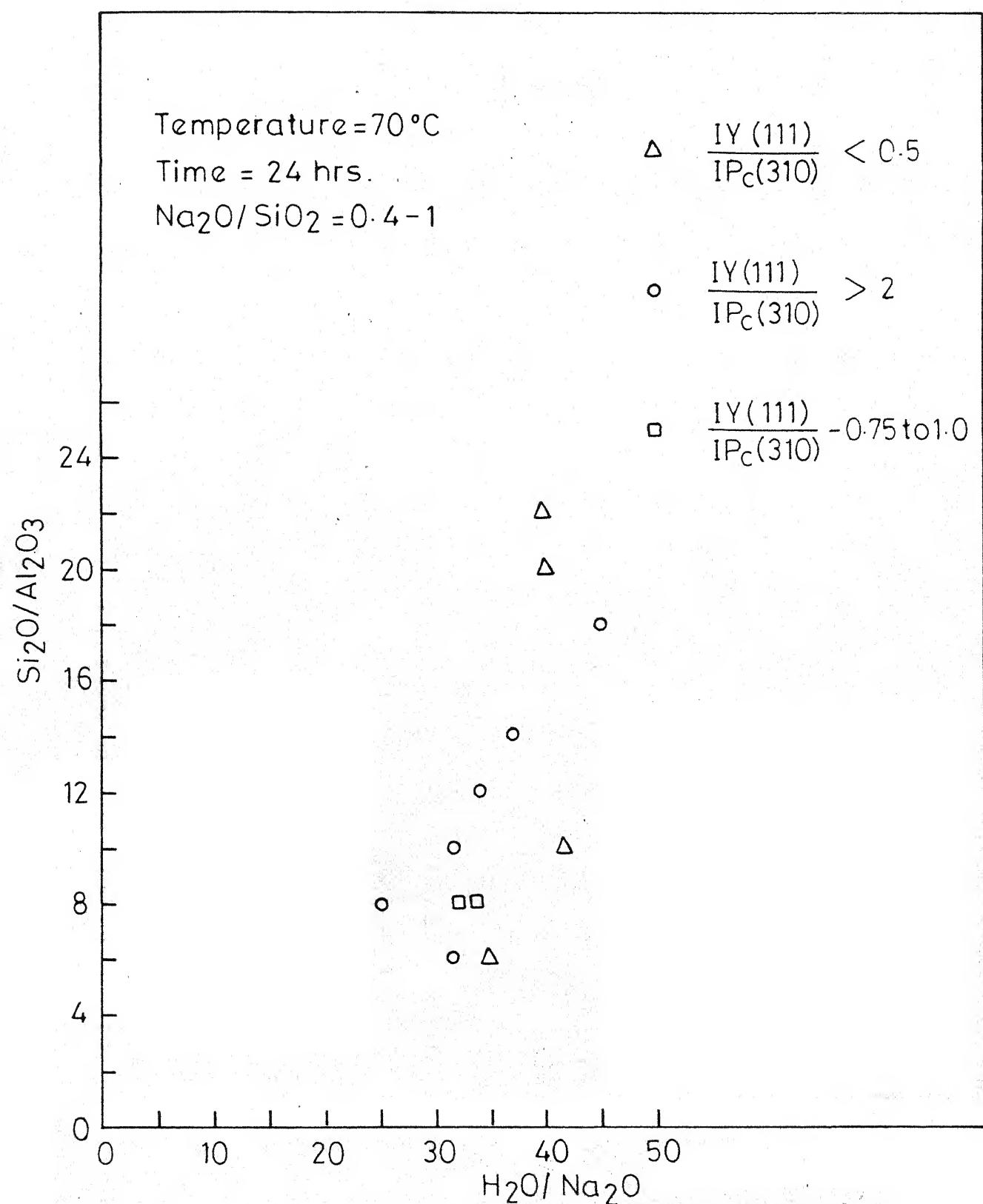
Fig. 4·11 – Effect of composition.

the only product and even traces of zeolites Y or P_c or analcime are absent. When colloidal silica is used in the form of silica gel to raise the silica content in the gel, zeolites Y, P_c and analcime resulted in the product depending upon the composition of the starting mix.

Influence of the composition of the starting mix has been clearly evidenced in the nature of the product with the ratio Na_2O/Al_2O_3 decreasing, the crystallization of zeolite Y is more (as with Na_2O/Al_2O_3 around 6 and 7) with particular values of SiO_2/Al_2O_3 (Run Nos. 1112 and 1211). When Na_2O/Al_2O_3 ratio decreased below 6 zeolite P_c has been the dominating species compared to the species Y. Thus pH appears to be the deciding factor for the crystallization of zeolite Y.

When SiO_2/Al_2O_3 was decreased for the same Na_2O/Al_2O_3 values zeolite Y dominated over the zeolite P_c at one stage (Run No.s 1112 and 1211) and decrease of SiO_2/Al_2O_3 ratio below 10. did not result in any further increase of zeolite Y in the product. (Table 4.1 run nos. 1012, 1212, and 1513).

With the water content of the gel increasing upto H_2O/Al_2O_3 mole ratio 200 the crystallization seems to favour zeolite Y. However, with further increase (beyond 200) zeolite P_c is the dominating species. For example, while the product was amorphous in the case of the mix with H_2O/Al_2O_3 mole ratio 170 (run 1811), zeolite Y is the

was the dominant species in the product for run no. 1211 with H_2O/Al_2O_3 200. With further increase of the H_2O/Al_2O_3 mole ratio to 250 (run No. 2011), zeolite P_c is the dominant constituent in the product.

It has been observed in the case of crystallization of zeolite Y, increase in the reaction time (beyond 48 hours) resulted in the formation of zeolite P_c at the expense of zeolite Y formed earlier. This trend can be clearly visualized by comparing the products in run nos. 911 with 912, 913 and 914 o or by comparing the products in the group of runs 711, 712, 713 and 714 (Table 4.1).

Synthesis at 80°C

As shown in Table 4.2, at 80°C either P_c is present to a considerable extent or the product is a mixture of all the three species zeolite Y, zeolite P_c and analcime.

Synthesis at 100°C

At 100°C, the limited number of runs conducted have revealed the products to be zeolites P_c and analcime. The species Y has been conspicuously found to be absent.

Thus zeolites Y, P_c and analcime can be relegated to the phases a, b and c respectively of Figure 2.1. It has been noticed that the transformation takes place from Y to P_c and P_c to analcime at 70°C and 100°C respectively. These temperature values are lower than the ones (100°C and 175°C)

TABLE 4.2: RESULTS OF TYPICAL RUNS: TEMPERATURE 80°C

Run No.	Reactant composition (moles/Al_2O_3)			Time hrs.	Intensity				
	Na_2O	SiO_2	H_2O		Y (111)	P_c (310)	An (400)	HS (211)	$\frac{Y(111)}{P_c(310)}$
523	8.0	20.0	320	60	—	4.5	1.0	—	—
524	8.0	20.0	320	72	—	3.1	0.45	—	—
623	9.0	22.0	360	48	—	1.9	—	—	—
624	9.0	22.0	360	72	0.5	1.3	0.05	—	0.38
722	7.0	18.0	315	48	1.9	1.6	0.25	—	1.19
723	7.0	18.0	315	60	2.7	1.5	0.3	—	1.8
724	7.0	18.0	315	72	2.8	2.1	1.3	—	1.33
922	7.0	14.0	260	18	0.5	—	—	—	—
923	7.0	14.0	260	24	6.8	2.1	—	—	3.23
924	7.0	14.0	260	36	6.0	2.7	0.7	—	2.22

reported by Breck (1974). Further the SiO_2/Al_2O_3 ratio
in the starting mixture needed for the synthesis of zeolite Y
is less in the case where rice husk ash is used than in the
case where sodium silicate was the main source of silica.
This can be attributed to the chemically reactive nature of the
silica obtained from rice husk ash.

CHAPTER 5

CONCLUSIONS

The present study has established that rice husk ash, can be used as a potential source of silica in the synthesis of zeolite species Y, in the Na_2O Al_2O SiO_2 H_2O system. In the agricultural countries like India, with the emphasis on rural technology, rice husk ash offers immense scope as a raw material for the zeolite manufacture So far, no attempt has been made in the utilization of this material in the synthesis of zeolite Y.

Within the ranges of variation for the composition, reaction temperature and the time, distinct trends for the crystallization of the zeolite Y and the associated species have been noticed. Zeolite Y was found to be the dominating species in the product when the composition of the starting material was maintained at 6 Na_2O Al_2O_3 10 SiO_2 200 H_2O.

If the participating silica content is less, hydrated sodalite has been evidenced.

When the mole ratios Na_2O/Al_2O_3 is greater than 7 and SiO_2/Al_2O_3 is in the range 14-20 and H_2O/Al_2O_3 is in the range of 200-260, zeolite P_c and analcime were found to be the dominating products.

The temperature levels for the transformation of zeolite Y and P_c and analcime have been found to be 70 and 100°C respectively. These temperature levels, obtained in the present case using rice husk ash as the main silica source, defer from the respective temperature levels (100°C and 175°C) indicated by earlier workers using silica chemicals.

The trends of crystallization of zeolites Y and P_c and analcime have been found to be in confirmation with the free energy vs temperature diagram proposed by Fyfe (1960).

Even after narrowing down the ranges of the composition, time and temperature during the synthesis in as many as 200 runs, it was not possible to accomplish the synthesis of the pure enmembers namely the zeolites Y and P_c. It appears that this can be accomplished by seeding the mix with the pure crystals of the species.

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APPENDIX

APPENDIX A

X-RAY POWDER DATA FOR ZEOLITE Y
(Breck, 1974)

hkl	d(A)	I
111	14.29	100
220	8.75	9
311	7.46	24
331	5.68	44
333, 511	4.76	23
440	4.38	35
620	3.91	12
533	3.775	47
444	3.573	4
711, 551	3.466	9
642	3.308	37
731 553	3.222	8
733	3.024	16
822, 660	2.917	21
751, 555	2.858	48
840	2.767	20
911, 753	2.717	7
664	2.638	19
931	2.595	11

APPENDIX B

X-RAY POWDER DATA FOR ZEOLITE P
(Breck, 1974)

Zeolite P$_c$			Zeolite P$_t$		
hkl	d(A)	I	hkl	d(A)	I
110	7.10	55	110	7.132	85
200	5.01	35	101	7.047	83
211	4.10	55	111	5.776	5
310	3.16	100	200	5.048	51
321	2.67	55	002	4.914	26
400	2.52	5	102	4.420	8
411,	2.36	7	211	4.108	94
330			112	4.049	22
422	2.054	5	202	3.527	4
510,	1.965	10	212	3.328	18
431			310	3.194	100
440	1.771	7	103	3.117	64
530,	1.719	7	311	3.036	10
433			113	2.979	5
600	1.667	7	302	2.776	3
422			203	2.750	5
			321	2.694	46
			312	2.679	28
			213	2.653	21
			400	2.531	6
			322	2.435	5
			104	2.387	4
			420,	2.257	2
			402		
			421	2.206	2
			214	2.159	2
			422	2.055	1
			510	1.982	2
			413	1.966	2
			105	1.929	1

APPENDIX C

X-RAY POWDER DATA FOR ANALCIME
(Breck, 1974)

hkl	d(A)	I	hkl	d(A)	I
200	6.87	10	761	1.480	20
211	5.61	80	664	1.463	10
220	4.86	40	754	1.447	10
321	3.67	20	932,	1.415	40
400	3.43	100	763		
332	2.925	80	941,	1.386	10
422	2.801	20	853		
431	2.693	50	860	1.372	10
521	2.505	50	1011	1.359	40
440	2.426	30	1031	1 308	10
611,	2.226	40	871	1.285	20
532			1033	1.263	20
620	2.168	10	963	1.220	30
541	2.115	10			
631	2.022	10			
543	1.940	10			
640	1.903	50			
633	1.867	40			
642	1.833	10			
732,	1.743	60			
651					
800	1.716	30			
741	1.689	40			
820	1.664	10			
822,	1.618	20			
660					
831,	1.596	30			
743					
842	1.498	20			